

12

# EUROPEAN PATENT APPLICATION

21 Application number: 86116907.6

51 Int. Cl.<sup>4</sup>: H 01 M 10/39

22 Date of filing: 04.12.86

30 Priority: 06.12.85 JP 273441/85

43 Date of publication of application:  
10.06.87 Bulletin 87/24

64 Designated Contracting States:  
DE FR GB

71 Applicant: HITACHI, LTD.  
6, Kanda Surugadai 4-chome  
Chiyoda-ku Tokyo 101(JP)

71 Applicant: Hitachi Engineering Co., Ltd.  
2-1, Saiwai-cho 3-chome  
Hitachi-shi Ibaraki 317(JP)

72 Inventor: Hoshino, Satoshi  
16-8 Asahi-cho 3-chome  
Hitachi-shi(JP)

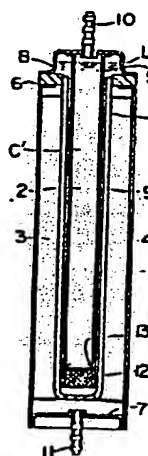
72 Inventor: Wada, Motoi  
5-2-402 Nishinarusawacho-1-chome  
Hitachi-shi(JP)

74 Representative: Strehl, Schübel-Hopf, Groening, Schulz  
Widenmayerstrasse 17 Postfach 22 03 45  
D-8000 München 22(DE)

54 Sodium-sulfur battery.

57 The present invention relates to an internal structure of cathode of a sodium-sulfur battery, and particularly to a sodium-sulfur battery which is improved to extend its life by keeping low the resistivity of sodium ion conductive solid electrolyte (1) through elimination of impurities in sodium which acts as a cathode active substance (2). That is, although it has hitherto been known that the solid electrolyte (1) is deteriorated by impurities such as  $K^+$ ,  $Ca^{2+}$  and the like in sodium which is the cathode active substance (2), a method for improving this has not been known. According to this invention, a porous adsorbent (12) is immersed in sodium which is the cathode active substance (2) to eliminate the impurities in the sodium, resulting in extension of the battery life.

FIG. 1



EP 0 224 932 A2

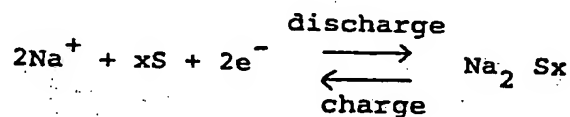
SODIUM-SULFUR BATTERY

1 BACKGROUND OF THE INVENTION

The present invention relates to an internal structure of a cathode of sodium-sulfur battery, and particularly to a sodium-sulfur battery which is improved to extend the life by keeping low resistivity of sodium ion conductive solid electrolyte through elimination of impurities in sodium which acts as a cathode active substance.

The sodium-sulfur battery is a high-temperature secondary battery in which the solid electrolyte permitting only sodium ion to pass through is interposed such that molten (liquid) sodium acting as a cathode active substance is disposed in one side and molten sulfur acting as an anode active substance is disposed in the other side, whereby charge and discharge may be carried out at a temperature range of about 300°C to 350°C.

Such charge and discharge reactions are represented by:



20 In discharge, an atomic sodium as the cathode active substance liberates electrons to become sodium ion, which passes through the barrier of the solid electrolyte to

- 2 -

1 react with the sulfur of the anode active substance and  
to produce the sodium polysulfide ( $\text{Na}_2 \text{S}_x$ ). In charge,  
the sodium polysulfide ( $\text{Na}_2 \text{S}_x$ ) is separated to the  
sodium (Na) and the sulfur (S) by applying the negative  
5 voltage larger than the voltage of opened circuit.

Fig. 2 illustrates an example of the conventional sodium-sulfur battery. Referring to the drawing, the sodium-sulfur battery consists of the molten sodium  
2 of the cathode active substance and the molten sulfur  
10 3 of the anode active substance filled inside and  
outside of a tubular solid electrolyte 1, respectively.  
Since the molten sulfur 3 has no electronic conductivity,  
a porous carbon fiber is impregnated with the molten  
sulfur 3 in order to give the electronic conductivity  
15 thereto. An anode container 4 in which the molten  
sulfur 3 is enclosed and a cathode tube 5 in which the  
molten sodium 2 is enclosed have the function of  
electrode, respectively, and the anode container 4 and  
the cathode tube 5 are connected in an insulated  
20 manner by an  $\alpha$ -alumina 6 which acts an insulating  
material.

Also, an anode cap 7 secured to the anode  
container 4 and a cathode cap 8 secured to the cathode  
tube 5 have the function of electrode as well as the  
25 anode container 4 and the cathode tube 5. A porous  
metal fiber 9, which is inserted into the molten  
sodium 2, has the function of retainer of the molten  
sodium 2 for preventing a drastic exothermic reaction

1 of the molten sodium 2 and the molten sulfur 3 when the  
solid electrolyte 1 is broken. To the cathode cap 8 is  
secured a sodium injection tube 10 for injecting sodium  
into the cathode tube 5. "C" designates a cathode  
5 which consists of the molten sodium 2 and the metal  
fiber 9. "L" designates a liquid surface of the sodium  
2. The solid electrolyte 1 in the sodium-sulfur  
battery is a main part which influences the performance  
of battery, and materials called  $\beta$ -alumina or  $\beta''$ -alumina  
10 are used as such electrolyte, which can be produced by  
mixing  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$  and the like with usual alumina  
powder, ~~molding the mixture under~~ an elevated pressure,  
followed by sintering at a high temperature. As to the  
characteristics of the solid electrolyte 1 for the  
15 sodium-sulfur battery, it is required that it has high  
density and no gas permeability, the mechanical strength  
is high, the ion conductivity is large, the resistance  
of grain boundaries (which means that the  
flow of sodium is biased between the grains so that  
20 it is hard to flow.) is low and the electric conductiv-  
ity is good, the distribution of grain size is  
uniform, and the grain is fine and not deteriorative.  
The main cause of deterioration of the solid electrolyte  
1 which has the particular characteristics as mentioned  
25 above, is the influence of impurities such as potassium  
ion ( $\text{K}^+$ ), calcium ion ( $\text{Ca}^{2+}$ ) and the like contained in  
the molten sodium 2.

The electric conductivity of the solid

- 4 -

1 electrolyte 1 with respect to the sodium ion ( $\text{Na}^+$ ) is  
deteriorated remarkably due to the existence of  
impurity ions ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ , etc.) contained in the molten  
sodium 2 as mentioned above, resulting in the high  
5 internal resistance of battery. Also, in the crystal  
structure of the solid electrolyte 1 ( $\beta$ - $\text{Al}_2\text{O}_3$ ,  $\beta''$ - $\text{Al}_2\text{O}_3$  or the like) consisting of the sodium ion ( $\text{Na}^+$ ),  
the substitution of the sodium ion ( $\text{Na}^+$ ) by the  
impurities ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ , etc.) causes the change of volume  
10 of the crystal single particle. The change of volume  
results in that stress is produced inside of the solid  
electrolyte 1 or near the surface thereof so that it  
accelerates the deterioration of the solid electrolyte  
1 because the crystal particles are different in size  
15 from the point of probability theory.

The deterioration mechanism of the solid  
electrolyte used for the sodium-sulfur battery is due  
to the damage when the sodium ion permeates through or  
to the action such as extreme increase of resistance.  
20 These are much influenced by the impurities contained  
in the sodium.

The deterioration phenomena of the solid  
electrolyte due to the impurities are described in the  
"Kagaku Kogyo" (Chemical Industries), August, 1980, page  
25 88, " $\beta$ -alumina (2)". However, it refers to neither the  
countermeasure nor the method of improvement for such  
deterioration.

Furthermore, the Japanese Patent Publication

- 5 -

1 No. 8552/83 discloses the improvements of strength and  
non-corrosiveness of the solid electrolyte for sodium-  
sulfur battery, but it describes neither the influence  
due to the impurities in sodium nor the method of  
5 improvement.

## SUMMARY OF THE INVENTION

This invention has been done in view of the  
above mentioned circumstances, and is aimed to provide  
a sodium-sulfur battery in which the sodium ion  
10 conductive solid electrolyte is prevented from deterior-  
ation, whereby the battery life is remarkably extended.

Next, the basic principle of this invention  
is described.

The life of the whole system of sodium-sulfur  
15 battery is often decided by deterioration phenomenon of  
the sodium ion conductive solid electrolyte itself.  
That is, the solid electrolyte through which a certain  
quantity of electric current has passed, sometimes  
generates micro-cracking or shows an action that the  
20 value of resistance increases extremely. Thus, in the  
deteriorated sodium-sulfur battery, the solid electro-  
lyte is easy to break and at the time of breakdown, the  
sodium which has high chemical reactivity reacts with  
sulfur in a short time to produce exothermic heat.  
25 This is not preferable from an aspect of safety. One  
of the causes of deterioration of the solid electrolyte  
used in the sodium-sulfur battery is largely due to

1 the influence of impurity contained in the sodium.  
Even the high purity sodium contains a very small  
amount of impurities such as potassium, calcium,  
hydrogen, oxygen boron and the like. These impurities  
5 change the composition of the solid electrolyte and the  
volume of crystal particle by substituting for the  
sodium ion and at this time, a stress occurs near the sur-  
face where many single crystal grains whose composition  
has been changed exist, and it breaks the solid elec-  
10 trolyte. Further, the impurities have properties that  
they penetrate into the grain boundaries of  
the solid electrolyte to increase the resistance of  
grain boundaries and to accelerate the  
deterioration and damage in the grain bound-  
15 aries. Accordingly, it is necessary for improving  
the battery life to eliminate the impurities present in  
sodium. Also, a marked extension of battery life can  
be expected by eliminating the impurities mentioned  
above. For achievement of the above-mentioned object,  
20 i.e. the extension of battery life by preventing the  
ion conductive solid electrolyte from deterioration,  
based on the principle described above, the sodium-  
sulfur battery of this invention is characterized in  
that a porous adsorbent is immersed in the sodium which  
25 acts as a cathode active substance.

As the porous adsorbent, porous adsorbents  
such as carbon, graphite, alumina and the like, and  
high purity porous active carbon are preferable.

1 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic illustration in cross section of an embodiment of sodium-sulfur battery according to this invention; and

5 Fig. 2 is a diagrammatic illustration in cross section of an example of the conventional sodium-sulfur battery.

10

DESCRIPTION OF THE PREFERRED EMBODIMENT OF THE INVENTION

15 Fig. 1 shows an embodiment of this invention. In Fig. 1, numeral 1 designates a  $\beta$ "-alumina solid electrolyte which has high electric conductivity with respect to sodium ion. Since the solid electrolyte 1 has high insulation property with respect to the elec-  
20 tronic conductivity, it retains separately sodium 2 which is a cathode active substance and sulfur 3 which is an anode active substance without self-discharging. The sodium in a solid electrolyte tube is separated into a sodium ion and an electron on the surface of  
25 solid electrolyte. When an external circuit is not connected between a cathode and an anode of the battery, the sodium ion does not transfer because of the negation



1 of electric field due to the space charge potential, but  
when there is a path electrically connecting between the  
cathode and the anode outside, the sodium ion can  
transfer to the sulfur electrode in the solid electro-  
5 lyte. The sodium ion, which has moved from the solid  
electrolyte into the sulfur electrode, excites the  
sulfur existing in the anode. The excited sulfur is  
going to absorb the surrounding free electrons so as  
to change itself to a bivalent negative ion, and at this  
10 time it generates potential energy of about 2.08 volts.  
The smooth supply of electrons to the anode is indis-  
pensable for continuously maintaining such reaction of  
battery. Therefore, in the anode a felt-like carbon  
fiber, which has large surface, high non-corrosiveness  
15 and good permeability of electron, is disposed to retain  
the sulfur by impregnation. In such anode, since  
sodium polysulfide which has high metal-corrosiveness  
is produced with the progress of battery reaction, a  
chromized steel which has high non-corrosiveness against  
20 the sodium polysulfide, is used for a container 4 of the  
anode active substance.

As mentioned above, the sodium transfers from  
the inside of the solid electrolyte tube to the outside  
at the time of discharge reaction of battery. There-  
25 fore, the discharge of battery terminates when the  
sodium is used up. At the time of charge, on the  
contrary, the sodium polysulfide in the anode is  
decomposed into the sodium ion, the sulfur and the

1 electron, and the sodium ion transfers in the solid  
electrolyte in accordance with the electric field  
produced by the voltage applied to the external circuit,  
and returns into the cathode. That is, the electrical  
5 capacity of the sodium-sulfur battery is determined by  
the quantity of sodium existing in the cathode. If  
the operating temperature of battery is low, the sodium  
polysulfide produced at the time of discharge reaction  
is solidified, and therefore the internal resistance  
10 increases and the energy efficiency is reduced. On the  
other hand, if the temperature is too high, the  
troubles of high-temperature corrosion, thermal stress  
and so on are caused. Therefore, the operating temper-  
ature of 300°C to 350°C is suitable.

15 At the operating temperature as mentioned  
above, the resistivity of  $\beta$ "-alumina which is the solid  
electrolyte is about 3 to 5  $\Omega$ cm. The internal resist-  
ance of battery consists of the resistances of the solid  
electrolyte, anode portion and cathode portion. As to  
20 the structure of the cathode portion, it is important  
for improvement of efficiency to make the internal  
resistance lower, and it is particularly important to  
flow the sodium ion uniformly over the region of the  
solid electrolyte. The reason is that the solid elec-  
25 trolyte has the property deteriorated by electric  
current and the rate of deterioration is proportionate  
to the density of electric current. That is, in the  
portion where the electric current flows more than

1 the other portions the electrolyte is damaged more, and  
the life of the whole solid electrolyte is defined by  
the portion where the current is concentrated. In order  
to flow the electric current uniformly over the region  
5 of the solid electrolyte, it is necessary that all of  
the cathode surface of the solid electrolyte is in  
contact with the sodium. However, since the quantity  
of sodium in the cathode is increased or decreased by  
the charge or discharge reaction, the liquid surface of  
10 sodium changes. Therefore, in the embodiment the  
cathode tube 5 is disposed in the solid electrolyte  
tube to form a double tube structure and in addition  
the region between the cathode tube and the solid  
electrolyte tube is filled with metal fiber 9. As to  
15 the metal fiber, a felt of stainless material, diameter  
of which is not more than 30  $\mu\text{m}$ , is preferable because  
it has good wettability to sodium, hence the effect of  
capillarity is enhanced, and also it has good non-  
corrosiveness. The sodium is absorbed upward by surface  
20 tension in the metal fiber and is supplied to all of the  
internal wall of the solid electrolyte.

When the battery which has the above structure  
is manufactured, the sodium as the cathode active  
substance is injected into the solid electrolyte through  
25 a sodium injection tube 10, and then it is enclosed.  
Though the sodium to be injected is produced in advance  
by eliminating K and Ca by purification methods such as  
distillation and adsorption methods, these impurities

1 are existing in large quantities on the ground and  
there is a great possibility that the impurities adhere  
to the surface of the cathode component material. In  
fact, in the battery which does not have the structure  
5 according to this invention, as a result of checking  
up the solid electrolyte after the charge and discharge  
of about 100 cycles, the amount of Ca as the impurity  
increased about four times. That is, the impurities  
intermingled in the cathode at the time of manufacture  
10 move in the solid electrolyte with the sodium and are  
captured therein. These impurities are built-up in the  
solid electrolyte by replacing the sodium which forms a  
crystal of the solid electrolyte. At that time, the  
change of component causes change of the crystal  
15 structure of the solid electrolyte and deformation of  
the crystal. Therefore, stress is generated in the  
electrolyte to cause micro-cracking. In addition, since  
the solid electrolyte in which the impurities are built-  
up increases the resistance, it deteriorates in  
20 efficiency to become unsuitable for practical use even  
if it would not be broken. Accordingly, a method of  
enclosing in the cathode a substance for eliminating  
impurities is desirable for manufacturing the battery  
which is good in performance and life.

25 In the embodiment of Fig. 1, the elimination  
of impurities as mentioned above is realized by an  
adsorbing action of porous amorphous carbon 12 which is  
disposed in the bottom of the cathode tube 5. The carbon

1 was manufactured by The Fluorocarbon Company, Anaheim,  
California 92803, U.S.A. Though there are various kinds  
of porous amorphous carbon now, one having a specific  
surface area of  $2500 \text{ m}^2/\text{g}$  was used. When the specific  
5 surface area is so large as above, the amount of the  
carbon to be used can be much smaller. The reason is  
that an ability of adsorbing the impurities is propor-  
tionate to the surface area of carbon material. When  
the above material was used, the impurities were  
10 eliminated satisfactorily (0.5 ppm, a limit of detec-  
tion, or less) only by use of about 50mg of carbon per  
100g of sodium.

As the carbon materials which have large  
specific surface area, there is provided a graphite felt  
15 material which can be obtained by heat treating a raw  
material of fiber at  $2500^\circ\text{C}$  or more. However, this  
can't give an effect comparable to the amorphous carbon  
because of smaller specific surface area by one figure,  
lower purity and so on.

20 In use of the amorphous carbon in sodium, it  
is important that the whole body of the carbon is in  
the sodium in addition to the maintainance of high  
purity as mentioned above. Since the amorphous carbon  
has small pores and air bubbles or the like can't  
25 easily escape upward if it adheres to the carbon, there  
is a possibility that the carbon floats on the liquid  
surface of sodium. If the amorphous carbon floats,  
the surface area of the carbon in which it is in contact

1 with the sodium is reduced, so this is undesirable.  
Accordingly, it is required to always secure the carbon  
in the sodium. In the embodiment, a holding projection  
13 secures the carbon in the bottom of the cathode  
5 tube. This position is set in a path through which  
the sodium is fed to the solid electrolyte tube, and  
also in a place where the sodium flows with the electric  
charge and discharge. In addition, it is most prefer-  
able as a position where the carbon is disposed because  
10 the carbon keeps in contact with the sodium until the  
discharge terminates. When the sodium moves in the  
place where the carbon exists, the impurities which are  
eliminated fundamentally by diffusion can also be  
eliminated by flow effect through a filter, thus the  
15 above disposition of carbon is preferable for elimination  
of impurity.

The sodium-sulfur battery which has the  
structure as mentioned above continues stable charge  
and discharge without increase of internal resistance  
20 even if the charge and discharge are generated at more  
than a few hundred cycles. On the contrary, in the  
battery which does not use the amorphous carbon the  
increase of internal resistance is remarkable, and it  
is found, as a result of analysis and check up after  
25 examination, that the amount of impurities in the solid  
electrolyte increased. That is, the performance and  
life of battery can be improved by elimination of  
impurities through the amorphous carbon.

1           As set forth hereinabove, according to this  
invention, it is possible to adsorb the impurities in  
sodium to be harmless, and therefore the deterioration  
of solid electrolyte is prevented so that the life of  
5 battery can be remarkably extended.

CLAIMS:

1. A sodium-sulfur battery comprising sodium as a cathode active substance (2) and molten sulfur or molten sodium polysulfide impregnated to a porous and electrically conductive material as an anode active substance (3), which  
5 effects electrochemical reactions of said cathode active substance (2) and said anode active substance (3) to charge or discharge through a solid electrolyte (1) having conductivity only for sodium ion, characterised in that a porous adsorbent (12) is immersed in said sodium as cathode active  
10 substance (2).
2. The battery of claim 1, wherein said porous adsorbent (12) is a substance having a function of adsorbing to a surface thereof alkali metal except sodium and/or alkali earth metal which have electrochemically positive polarity  
5 and act as an impurity in sodium.
3. The battery of claim 2, wherein said porous adsorbent (12) is porous amorphous carbon.
4. The battery of claim 2, wherein said impurity in sodium is potassium ion ( $K^+$ ) and/or calcium ion ( $Ca^{2+}$ ).
5. The battery of claim 1, wherein said porous adsorbent (12) immersed in said sodium is disposed near the closed bottom of tubular solid electrolyte (1) filled with said sodium as cathode active substance (2).



1/1

0224932

FIG. 1

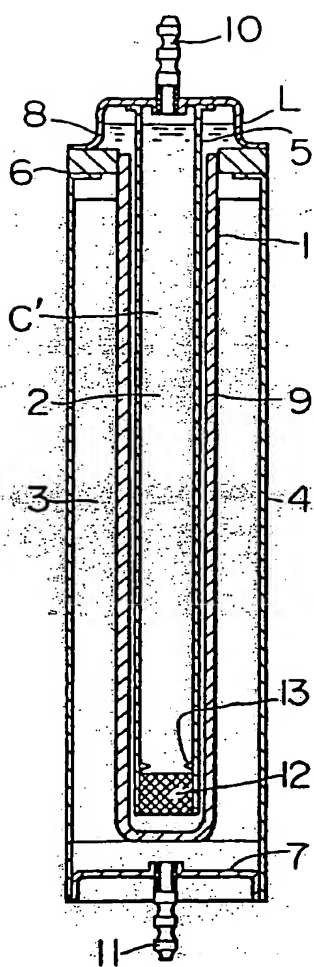


FIG. 2

